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## INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

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<b>(21) International Application Number:</b> PCT/US94/07232 <b>(22) International Filing Date:</b> 24 June 1994 (24.06.94)  <b>(30) Priority Data:</b> 141,911 22 October 1993 (22.10.93) US  <b>(71) Applicant:</b> MOBIL OIL CORPORATION [US/US]; 3225 Gallows Road, Fairfax, VA 22037-0001 (US).  <b>(72) Inventors:</b> LO, Frederick, Yip-Kwai; P.O. Box 752, Edison, NY 08818 (US). PRUDEN, Ann, Lorette; R.D. 2, 21 Harlingen Road, Bellemead, NJ 08502 (US).  <b>(74) Agents:</b> SUNG, Tak, K. et al.; Mobil Oil Corporation, 3225 Gallows Road, Fairfax, VA 22037-0001 (US).		<b>(81) Designated States:</b> AU, CA, JP, KR, European patent (AT, BE, CH, DE, DK, ES, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE).  <b>Published</b> <i>With international search report.</i>
<b>(54) Title:</b> AN OLEFIN POLYMERIZATION OR COPOLYMERIZATION CATALYST  <b>(57) Abstract</b>  An olefin polymerization or copolymerization catalyst comprising particles. The particles comprise silica, a transition metal and aluminum. The silica is amorphous, porous, has a pore volume of 0.1 to 5 cm <sup>3</sup> /g and has a concentration of silanol groups which is at least 0.7 mmole per gram of silica. The transition metal and the aluminum are provided by a mixture of a metallocene and an alumoxane. The total volume of the metallocene and said alumoxane is less than or equal to the total pore volume of the silica.		

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### An Olefin Polymerization or Copolymerization Catalyst

This invention relates an olefin polymerization or copolymerization catalyst; it also relates to a method for making such a catalyst.

This sort of catalyst comprises metallocenes of transition metals, and is characterized by extremely high activity. The catalyst of the invention operates smoothly in both the gas phase, e.g. fluid bed, and in slurry polymerizations. The catalyst can produce high molecular weight polymer at temperature and pressure conditions typically found in a commercial fluid bed reactor. Moreover, the catalyst can yield high bulk density, granular linear low density polyethylene in slurry polymerizations without reactor fouling.

The polymer products generally have narrow molecular weight distribution, are free of gels, and, for linear low density have homogeneous comonomer distribution. Reactor fouling is eliminated in both gas phase fluid bed and slurry polymerizations.

Polyethylene is produced commercially in a gas phase reaction in the absence of solvents by employing selected chromium and titanium-containing catalysts under specific operating conditions in a fluid bed process. Polyethylene products of the original processes exhibited medium-to-broad molecular weight distribution. To be commercially useful in the gas phase fluid bed process, or slurry reactor process, undertaken at low pressures less than about 1000 psi (6.89 MPa), the catalyst must exhibit high activity, with concomitant high catalyst productivity, because these process systems do not include catalyst residue removal procedures. Accordingly, catalyst residue in the polymer product must be so small that it can be left in the polymer without causing any undue problems in the fabrication and/or to the ultimate consumer. To this end, the patent literature is replete with developments of new catalysts.

The use of metallocene compounds of transition metals as catalysts for polymerization and copolymerization of ethylene

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is one of those developments. Metallocenes can be described by the empirical formula  $Cp_mMA_nB_p$ . These compounds in combination with methylalumoxane (MAO) have been used to produce olefin polymers and copolymers, such as ethylene and propylene homopolymers, ethylene-butene and ethylene-hexene copolymers, e.g., see US-A-4542199 and US-A-4404344.

Aluminoxanes, e.g. methylalumoxane (MAO), have been used as co-catalyst with metallocene catalysts. The class of aluminoxanes (used interchangeably hereinafter with "aluminoxane") comprises oligomeric linear and/or cyclic alkylaluminoxanes represented by the formula:

$R-(Al(R)-O)_n-AlR_2$  for oligomeric, linear aluminoxanes; and

$(-Al(R)-O)_m$  for oligomeric cyclic aluminoxane wherein  $n$  is 1-40, preferably 10-20,  $m$  is 3-40, preferably 3-20 and  $R$  is a  $C_1-C_8$  alkyl group and preferably methyl.

Methylalumoxane is commonly produced by reacting trimethylaluminum with water or with hydrated inorganic salts, such as  $CuSO_4 \cdot 5H_2O$  or  $Al_2(SO_4)_3 \cdot 5H_2O$ . Methylalumoxane can be also generated in situ in polymerization reactors by adding to them trimethylaluminum and water or water-containing inorganic salts.

MAO is a mixture of oligomers with a very wide distribution of molecular weights and usually with an average molecular weight of about 1200. MAO is typically kept in solution in toluene. While the MAO solutions remain liquid at fluid bed reactor temperatures, the MAO itself is a solid at room temperature.

The slow development of the metallocene catalysts has been in part attributable to the aluminoxane (hereinafter used interchangeably with "aluminoxane"). It was discovered that extensive reactor fouling results when MAO solutions are fed directly into the gas phase reactor in large enough quantities to provide this liquid contact with metallocene compound. The fouling occurs because the MAO solution forms a liquid film on

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the interior walls of the reactor. The catalyst is activated when it comes into contact with this liquid film, and the activated catalyst reacts with ethylene to form a polymer coating which grows larger in size until the reactor is fouled.

5 In addition, since substantially all of the activation takes place on the walls, the MAO is not uniformly distributed to the catalyst particles. The resulting non-homogeneous polymerization gives low catalyst activity and poor product properties.

10 The invention relates to a metallocene catalyst which does not require an aluminosilane co-feed to the polymerization reactor. Moreover, the catalyst of the invention exhibits high activity and productivity, in the fluid bed gas phase and slurry polymerization and copolymerization of olefins. (A-)

15 The problems invoked by the use of an aluminosilane, methylaluminosilane, in catalyst production are addressed by the catalyst of the invention, which comprises particles of silica, a transition metal and aluminum, wherein:

- 20 (a) wherein said silica is amorphous, porous; has a pore volume of 0.1 to 5 cm<sup>3</sup>/g and has a concentration of silanol groups wherein the concentration of silanol groups is at least 0.7 mmole per gram of silica;
- (b) said transition metal and said aluminum being
- 25 provided by a mixture of a metallocene and an aluminosilane; and
- (c) the total volume of said metallocene and said aluminosilane is less than or equal to the total pore volume of the silica.

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#### Catalyst Composition

The catalyst of the invention comprises a silica carrier, an aluminosilane and at least one metallocene. The catalyst is particulate in form, preferably comprising dry, free-flowing, powder particles having a particle size of from 1 to 500 microns, more preferably 1 to 250 microns, and most preferably from 10 to 150 microns.

The catalyst which preferably contains only one transition metal in the form of the metallocene has an activity of at least about 200 kg polymer/g of transition metals. The aluminoxane and metallocene loading on the carrier is preferably such that the amount of aluminum, (elemental basis) provided by the aluminoxane, on the carrier ranges from 1 to 40 weight percent, preferably from 5 to 30 weight percent, and most preferably from 5 to 15 weight percent. The optimum MAO loading is in the range of 3 to 15 mmoles per gram of silica carrier; if a silica carrier is overloaded with MAO, the catalyst activity is lower and the catalyst particles agglomerate with attendant problems of transferring the catalyst.

The amount of metallocene on the carrier, calculated on a transition metal (elemental basis), preferably ranges from 0.001 to 15 weight percent, more preferably from 0.5 to 0.3, and most preferably from 0.05 to 0.2 weight percent. Accordingly the ratio of Al:Zr (on an elemental basis) in the catalyst can range from 25 to 10,000, usually within the range of from 70 to 980 but preferably from about 70 to 350 or 100 to 350, and most preferably from 100 to 200.

The carrier material is preferably solid and particulate. In the most preferred embodiment, the carrier is silica in the form of spherical particles, e.g., as obtained by a spray-drying process. The carrier material is preferably used in the form of a dry powder having a particle size of from 1 to 500 microns, more preferably from 1 to 250 microns, and most preferably from 10 microns to 150 microns particle size.

If necessary, the final catalyst containing carrier material may be sieved to insure elimination of large catalyst particles. Presently, elimination of catalyst particles that have a particle size of greater than 500 microns is envisaged; preferably, elimination of particles of greater than 250 micron particle size, and, most preferably, elimination of particles of greater than 150 micron particle size is undertaken. Sieving of the material is preferably undertaken after impregnation of the carrier with the metallocene and the aluminoxane. This is highly desirable when the catalyst contains only one transition

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metal in the form of a metallocene, which is used to form narrow molecular weight LLDPE, to reduce and/or to eliminate gels in the final polyolefin product and to eliminate reactor hot spots, thereby to insure reactor continuity, particularly in the gas 5 phase fluid bed process.

The surface area of the carrier preferably is at least about 3 m<sup>2</sup>/g, more preferably, 5 to 1200 m<sup>2</sup>/g and most preferably at least about 50 m<sup>2</sup>/g up to about 350 m<sup>2</sup>/g. The pore volume of the carrier will range from 0.1 to 5 cm<sup>3</sup>/g, 10 preferably from 0.1 to 3.5 cm<sup>3</sup>/g. The carrier material should preferably be dry, that is, free of absorbed water.

The carrier material must have at least some active hydroxyl (OH) groups to produce the catalyst composition of this invention. The hydroxyl group concentration must be at least 15 about 0.7 mmole/gram silica. Preferably the hydroxyl group concentration is greater than 0.7 mmole/gram silica; more preferably it is at least 0.75 mmole/gram silica; and still more preferably it is at least 0.8 mmole/gram silica. The preferred upper limit for the hydroxyl group concentration is 2.5

20 mmoles/gram silica. In a particularly preferred embodiment the hydroxyl group concentration of the silica ranges from 1.6 to 2.5 mmoles/gram silica. This range is favored by slower drying, dehydration and/or calcination temperatures. The most preferred range is 1.6 to 1.9 mmoles hydroxyl groups/gram silica.

25 The silica hydroxyl (herein silanol, silica hydroxyl is used interchangeably) groups are detectable by IR spectroscopy. Quantitative determinations of the hydroxyl concentration on silica are made by contacting a silica sample with methyl magnesium iodide and measuring methane evolution (by pressure 30 determination).

Dehydration of silica material can be effected by heating at 100°C to 600°C, preferably from 150°C to 300°C and most preferably at 250°C.

By comparison, silica dehydrated at 600°C (for about 16 35 hours) will have a surface hydroxyl concentration of about 0.7 mmoles per gram (mmols/g) of silica. Silica dehydrated at 800°C will be a silica with 0.5 mmole of silica hydroxy per gram



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silica. The silica of the most preferred embodiment is a high surface area, amorphous silica (surface area =  $300 \text{ m}^2/\text{g}$ ; pore volume of  $1.65 \text{ cm}^3/\text{g}$ ), and it is a material marketed under the tradenames of Davison 952 or Davison 955 by the Davison Chemical Division of W. R. Grace and Company. As purchased, the silicas are not dehydrated, but they can be dehydrated prior to use.

The effect of silica hydroxyl groups on the catalyst activity and productivity is reflected in the EXAMPLES below.

The catalyst synthesis of the catalyst of the invention

exhibiting highest activity dictates that the silica contain

hydroxyl groups for contact with the solution containing

aluminoxane and metallocene, described below. It was determined

that reaction of the hydroxyl groups of the silica with

scavengers, such as trialkylaluminum compounds, e.g.,

trimethylaluminum (TMA), reduced the activity of the catalyst

produced thereby compared to a catalyst formed with a silica

having hydroxyl groups unreacted with such a scavenger. Silicas

containing higher hydroxyl numbers produce catalysts of higher

activity than silicas of lower hydroxyl numbers; US patent

application No 08/141912 it was shown that treating the silica

with trimethylaluminum to react with the silanol [which, with

appropriate molar amount of TMA the hydroxyl concentration is

reduced to zero, as indicated by IR (infrared)] prior to

catalyst synthesis produced a catalyst with a productivity of

about 200 kg (polymer)/g (transition metal). By comparison, the

catalysts produce herein with a hydroxyl group content of 1.8

mmole/gram silica exhibits a productivity of about 1000

kg (polymer)/g transition metal.

The amount of hydroxyl groups, in mmoles/gram silica can

be affected by the dehydration temperatures used to condition

the silica. Specifically, the dehydration temperatures of about

600°C reduce the amount of reactive hydroxyl groups available

for contact with the solution of aluminoxane and metallocene.

By comparison, the dehydration temperatures of about 250°C

increase the amount of reactive hydroxyl groups available for

contact with the solution of aluminoxane and metallocene,

relative to the silica heat treated, for dehydration purposes

the pores of the catalyst material without forming a silica

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to 600°C. Thus it has been found that the catalyst made with the silica subjected to dehydration temperatures of 250°C is more active than a catalyst produced with the silica subjected to drying temperatures of 600°C. Accordingly, preferred dehydration and/or calcination temperatures are below 400°C, more preferably below 300°C, and most preferably at about 250°C.

To form the catalyst of the invention, all catalyst components can be dissolved with alumoxane and impregnated into the carrier. Catalyst preparation is preferably undertaken under anhydrous conditions and in the absence of oxygen.

The carrier material can be impregnated with alumoxane, preferably methylalumoxane, in a process described below. The class of alumoxanes comprises oligomeric, linear and/or cyclic alkylalumoxanes represented by one of the formulae:

$R-(Al(R)-O)_n-AlR_2$  for oligomeric, linear alumoxanes; and  
 $(-Al(R)-O)_m$  for oligomeric cyclic alumoxanes  
wherein n is 1-40, preferably 10-20, m is 3-40, preferably 3-20 and R is a C<sub>1</sub>-C<sub>8</sub> alkyl group and preferably methyl.

MAO is a mixture of oligomers with a very wide distribution of molecular weights and usually with an average molecular weight of about 1200. MAO is typically kept in solution in toluene.

The volume of the solution comprising an alumoxane and a solvent therefor can vary, depending on the catalyst sought to be produced. In a preferred embodiment of alumoxane incorporation into the carrier, one of the controlling factors in the alumoxane incorporation into the carrier material catalyst synthesis is the pore volume of the silica. In this preferred embodiment, the process of impregnating the carrier material is by infusion of the alumoxane solution, without forming a slurry of the carrier material, such as silica, in the alumoxane solution. This is undertaken with agitation. The volume of the solution of the alumoxane is sufficient to fill the pores of the carrier material without forming a slurry in

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which the volume of the solution exceeds the pore volume of the silica; accordingly, the maximum volume of the alumoxane solution does not exceed the total pore volume of the carrier material. That maximum volume of the alumoxane solution ensures 5 that no slurry of silica in solvent is formed in this step.

By way of example, if the pore volume of the carrier material is  $1.65 \text{ cm}^3/\text{g}$ , then the volume of alumoxane will be equal to or less than  $1.65 \text{ cm}^3/\text{g}$  of carrier material. Thus, the maximum volume of solution (of metallocene and alumoxane) will 10 equal the total pore volume of the carrier, e.g. silica, which is the pore volume in, e.g.,  $\text{cm}^3/\text{g}$ , times the total weight of the carrier used. As a result of this provision, the impregnated carrier material will appear dry immediately following impregnation although the pores of the carrier may be 15 filled with inter alia solvent.

However, it has been noted that the solution volume can be up to 30% greater than the total pore volume of the silica with 20 the result(s) that no slurry of the silica is formed and that the silica remains dry in appearance. The preferred solvent for the aluminoxane, e.g. methaluminoxane, is toluene. The advantage is that the impregnation is undertaken in a single solvent system.

Solvent may be removed from the alumoxane impregnated pores of the carrier material by heating and/or under a vacuum or 25 purged with heating in an inert gas, such as nitrogen. If elevated temperature is employed, the temperature conditions in this step are controlled to reduce, if not to eliminate, agglomeration of impregnated carrier particles and/or crosslinking of the alumoxane. In this step, solvent can be 30 removed by evaporation effected at relatively low elevated temperatures of above about  $40^\circ\text{C}$  and below about  $50^\circ\text{C}$  to obviate agglomeration of catalyst particles and crosslinking of the alumoxane. Preferably drying is undertaken at  $45^\circ\text{C}$  or less for 5 to 7 hours.

35 Although solvent can be removed by evaporation at relatively higher temperatures than that defined by the range above  $40^\circ\text{C}$  and below about  $50^\circ\text{C}$ , very short heating times

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schedules must be employed to obviate agglomeration of catalyst particles and crosslinking of the alumoxane, with reduction of catalyst activity. Accordingly, an active catalyst has been produced at evaporation temperature of 110°C (at extremely short 5 heating times), whereas at 45°C, drying can be undertaken for periods of 24 hours.

In a preferred embodiment, the metallocene is added to the solution of the alumoxane prior to impregnating the carrier with the solution. Again the maximum volume of the alumoxane solution also containing the metallocene is the total pore volume of the carrier material sample. The mole ratio of aluminum provided by aluminoxane, expressed as Al, to metallocene metal expressed as M (e.g. Zr), preferably ranges from 50 to 500, more preferably 75 to 300, and most preferably

15 100 to 200. An added advantage of the present invention is that this Al:Zr ratio can be directly controlled.

In a preferred embodiment the alumoxane and metallocene compound are mixed together at ambient temperature for 0.1 to 6.0 hours, prior to use in the infusion step. The solvent for the metallocene and alumoxane can be appropriate solvents, such as aromatic hydrocarbons, halogenated aromatic hydrocarbons, ethers, cyclic ethers or esters; preferably it is toluene.

The metallocene compound has the formula  $CpMA_nB$ , in which Cp is an unsubstituted or substituted cyclopentadienyl group,

25 M is zirconium or hafnium and A and B belong to the group including a halogen atom, hydrogen or an alkyl group. In the above formula of the metallocene compound the preferred transition metal atom M is zirconium. In the above formula of the metallocene compound, the Cp group is an unsubstituted, a

30 mono- or a polysubstituted cyclopentadienyl group. The substituents on the cyclopentadienyl group can be preferably straight- or branched chain  $C_1-C_6$  alkyl groups. The cyclopentadienyl group can be also a part of a bicyclic or a

tricyclic moiety such as indenyl, tetrahydroindenyl, fluorenyl or a partially hydrogenated fluorenyl group, as well as a part of a substituted bicyclic or tricyclic moiety. In the case when m in the above formula of the metallocene compound is equal to

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2, the cyclopentadienyl groups can be also bridged by polymethylen or dialkylsilane groups, such as  $-CH_2-$ ,  $-CH_2-CH_2-$ ,  $-CR'R''-$  and  $-CR'R''-CR'R''-$  where  $R'$  and  $R''$  are short alkyl groups or hydrogen,  $-Si(CH_3)_2-$ ,  $-Si(CH_3)_2-CH_2-CH_2-Si(CH_3)_2-$  and similar bridge groups. If the A and B substituents in the above formula of the metallocene compound are halogen atoms, they belong to the group of fluorine, chlorine, bromine or iodine. If the substituents A and B in the above formula of the metallocene compound are alkyl groups, they are preferably straight-chain or branched  $C_1-C_8$  alkyl groups, such as methyl, ethyl, n-propyl, isopropyl, n-butyl, isobutyl, n-pentyl, n-hexyl or n-octyl.

Suitable metallocene compounds include bis(cyclopentadienyl)metal dihalides, bis(cyclopentadienyl)metal hydridohalides, bis(cyclopentadienyl)metal monoalkyl monohalides, bis(cyclopentadienyl)metal dialkyls and bis(indenyl)metal dihalides wherein the metal is zirconium or hafnium, halide groups are preferably chlorine and the alkyl groups are  $C_1-C_6$  alkyls. Illustrative, but non-limiting examples of metallocenes include bis(cyclopentadienyl)zirconium dichloride, bis(cyclopentadienyl)hafnium dichloride, bis(cyclopentadienyl)zirconium dimethyl, bis(cyclopentadienyl)hafnium dimethyl, bis(cyclopentadienyl)zirconium hydrido-chloride, bis(cyclopentadienyl)hafnium hydrido-chloride, bis(n-butylcyclopentadienyl)zirconium dichloride, bis(n-butylcyclopentadienyl)hafnium dichloride, bis(n-butylcyclopentadienyl)zirconium dimethyl, bis(n-butylcyclopentadienyl)hafnium dimethyl, bis(n-butylcyclopentadienyl)zirconium hydrido-chloride, bis(n-butylcyclopentadienyl)hafnium hydrido-chloride, bis(pentamethylcyclopentadienyl)zirconium dichloride, bis(pentamethylcyclopentadienyl)hafnium dichloride, bis(n-butylcyclopentadienyl)zirconium dichloride, cyclopentadienyl-zirconium trichloride, bis(indenyl)zirconium dichloride, bis(4,5,6,7-tetrahydro-1-indenyl)zirconium dichloride, and ethylene-[bis(4,5,6,7-tetrahydro-1-indenyl)]zirconium dichloride. The metallocene compounds utilized within the process of the present invention are not limited to the above examples.

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embodiment of this art can be used (as crystalline solids, as solutions in aromatic hydrocarbons or in a supported form). These catalysts are effective to form uniform blocks of  $\alpha$  olefins of 3 to 10 carbon atoms, in a polymer containing a predominant amount of polymerized ethylene. These catalysts are unique in that they do form uniform blocks of  $\alpha$  olefins of 3 to 10 carbon atoms, in a polymer containing a predominant amount of polymerized ethylene, in processes run at low pressures, up to, specifically no greater than, 400 psi (2.8 MPa), at temperatures up to 130°C.

These catalysts exhibit long catalyst life, high activity and productivity, and produce high bulk density products.

Conditions for the polymerization and copolymerization of ethylene

The process of the invention may be undertaken in gas phase, in fluid bed gas phase, or in slurry. The catalyst of the invention exhibits long catalyst life. The catalyst of the invention, allows for the production of linear low density polyethylene in the gas phase or in a slurry polymerization without reactor fouling. With respect to the slurry operation to produce LLDPE, particulate linear low density polyethylene is produced in the slurry reactor and is not swollen (by the solvent). The products from both the gas phase (e.g. fluid bed) and slurry have a high bulk density, which allows for increased throughput of product per weight of catalyst.

Preferably, the polymerization (copolymerization) is undertaken at a temperature and/or pressure below the sintering temperature of the polymer particles. Most preferably, the process is undertaken in the fluid bed gas phase or in a slurry reactor. The high activity of the catalysts herein allow for efficacious low pressure fluid bed gas phase and/or slurry process product production. Much lower activity catalysts than those described herein may be employed in high pressure processes at pressures which exceed 400 psi (2.8 MPa), such as solution and high pressure slurry polymerizations. For the production of ethylene copolymers in the process of the present

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invention an operating temperature of about 30°C to 115°C is preferred, and a temperature of about 70°C to 106°C is most preferred. Temperatures of about 75°C to 90°C are used to prepare products having a density of about 0.91 to 0.92, and 5 temperatures of about 80°C to 100°C are used to prepare products having a density of about 0.92 to 0.94, and temperatures of about 90°C to 115°C are used to prepare products having a density of about 0.94 to 0.96.

In the gas phase, linear low density production is 10 conducted at about 85°C and high density product is formed at about 105°C. In slurry polymerization, linear low density production is conducted at about 70°C and high density production is conducted at about 90°C.

In polymerizations described herein, pressures are below 15 10000 psi (69 MPa), preferably below 1000 psi (6.9 MPa). The fluid bed reactor is operated at pressures of up to about 1000 psi (6.9 MPa), and is preferably operated at a pressure of from about 150 to 350 psi (1.0 to 2.4 MPa), with operation at the higher pressures in such ranges favouring heat transfer since 20 an increase in pressure increases the unit volume heat capacity of the gas.

The partially or completely activated catalyst is injected 25 into the bed at a point above the distribution plate at a rate equal to its consumption. Since the catalysts used in the present invention are highly active, injection of the fully activated catalyst into the area below the distribution plate may cause polymerization to begin there and eventually cause 30 plugging of the distribution plate. Instead, injection into the bed aids in distributing the catalyst throughout the bed and precludes the formation of localized spots of high catalyst concentration.

The production rate of polymer in the bed is controlled by the rate of catalyst injection. Since any change in the rate 35 of catalyst injection changes the rate of generation of the heat of reaction, the temperature of the recycle gas is adjusted to accommodate the change in rate of heat generation. Complete instrumentation of both the fluidized bed and the recycle gas

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cooling system is, of course, necessary to detect any temperature change in the bed so as to enable the operator to make a suitable adjustment in the temperature of the recycle gas.

5 Since the rate of heat generation is directly related to product formation, a measurement of the temperature rise of the gas across the reactor (the difference between inlet gas temperature and exit gas temperature) is determinative of the rate of particulate polymer formation at a constant gas velocity.

10 The Fluid Bed Reactor

Reference is now made to the accompanying drawing, which is a schematic drawing of a fluid bed reactor for gas phase polymerization of ethylene.

A fluidized bed reaction system which can be used in the practice of the process of the present invention is shown in Fig. 1. With reference thereto, the reactor 10 consists of a reaction zone 12, a velocity reduction zone 14 and the distributor plate 20. Although fouling can occur in all of the

cold areas (areas in a reactor at a temperature which is less than the temperature at which any components, in the gas phase reactor is liquid rather than gaseous) distributor plate fouling is the one most easily detected, since it results in a rapid increase in the pressure drop across the distributor plate due to flow restriction. Such flow restrictions also result in changing fluidization patterns and contribute to reactor wall fouling. The lowest temperature in the reactor loop is in the reactor inlet beneath the distributor plate. Other areas representing the coldest sections in the fluid bed reactor

system include the cooler and piping between the cooler and the bottom head.

The reaction zone 12 comprises a bed of growing polymer particles and a minor amount of catalyst particles fluidized by the continuous flow of polymerizable and modifying gaseous components. To maintain a viable fluidized bed, the mass gas flow rate through the bed must be above the minimum flow



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required for fluidization, and preferably from about 1.5 to about 10 times Gmf and more preferably from about 3 to about 6 times Gmf. Gmf is used in the accepted form as the abbreviation for the minimum mass gas flow required to achieve fluidization (see C. Y. Wen and Y. H. Yu, "Mechanics of Fluidization", Chemical Engineering Progress Symposium Series, Vol. 62, p. 100-111 (1966)).

The distribution plate 20 serves the purpose of diffusing recycle gas through the bed at a rate sufficient to maintain fluidization at the base of the bed. Fluidization is achieved by a high rate of gas recycle to and through the bed, typically in the order of about 50 times the rate of feed of make-up gas. Make-up gas is fed to the bed at a rate equal to the rate at which particulate polymer product is formed by reaction. The composition of the make-up gas is determined by a gas analyzer 15 positioned above the bed. The composition of the make-up gas is continuously adjusted to maintain an essentially steady state gaseous composition within the reaction zone.

The portion of the gas stream which does not react in the bed (the recycle gas) passes a velocity reduction zone 14 where entrained particles are given an opportunity to drop back into the bed, through a cyclone 22, through a filter 24 (optionally) and is compressed in a compressor 25, passes through a heat exchanger 26 and is returned to the bed. The distribution plate 20 serves the purpose of diffusing recycle gas through the bed at a rate sufficient to maintain fluidization. The plate may be a screen, slotted plate, perforated plate, a plate of the bubble cap type, and the like. The elements of the plate may all be stationary, or the plate may be of the mobile type disclosed in US-A-3298792.

Under a given set of operating conditions, the fluidized bed is maintained at essentially a constant height by withdrawing a portion of the bed as product at a rate equal to the rate of formation of the particulate polymer product.

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#### The polymerization and copolymerization products

Both low density (0.91 to 0.939 g/cm<sup>3</sup>) and high density and more linear and of somewhat abrupt linearly

- 15 -

at 2.1 moles per mole of catalyst, and products with high bulk density, (0.94 to 0.965 g/cm<sup>3</sup> and above) products with high bulk density, low (hexane) extractables and granular morphology can be prepared in the slurry or gas phase reactor with no fouling. The resin produced has a high molecular weight, narrow molecular weight distribution, and homogeneous branching distribution. The catalyst ash contains small amounts of Zr and Al, e.g., less than 1 ppm Zr and 40 ppm Al. The high activity of the catalysts of the invention which also exhibit long catalyst life and produce high bulk density products are significant factors in the unexpected efficacy of these catalysts in catalytic polymerizations and copolymerizations of olefins.

Ethylene polymers, as well as copolymers of ethylene with one or more C<sub>3</sub>-C<sub>10</sub> alpha-olefins, can be produced in accordance with the invention. Thus, copolymers having two monomeric units are possible as well as terpolymers having three monomeric units. Particular examples of such polymers include ethylene/1-butene copolymers, ethylene/1-hexene copolymers and ethylene/4-methyl-1-pentene copolymers.

Since the catalyst is effective to incorporate comonomer in a regular manner the resin may contain blocks of polymerized product of alpha olefins of 3 to 10 carbon atoms in the resin backbone. These blocks will consist essentially of dimers, oligomers, polymers and admixtures thereof. Because of the excellent comonomer incorporation of the catalyst and the branching homogeneity of the resin, significant amount of hexene saving can be achieved.

Ethylene/1-butene and ethylene/1-hexene copolymers are the most preferred copolymers polymerized in the process of and with the catalyst of this invention. The ethylene copolymers produced

in accordance with the present invention preferably contain at least about 80 percent by weight of ethylene units. The cocatalyst of this invention can also be used with the catalyst precursor of this invention to polymerize propylene and other alpha-olefins and to copolymerize them. The structure of alpha-

olefin polymers prepared with the cocatalyst and the catalyst precursor of this invention depends on the structure of the cyclopentadienyl ligands attached to the metal atom in the

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catalyst precursor molecule. The cocatalyst compositions of this invention can also be used with the catalyst precursors of this invention to polymerize cycloolefins such as cyclopentene.

Hydrogen may be used as a chain transfer agent in the polymerization reaction of the present invention. The ratio of hydrogen/ethylene employed will vary between about 0 to about 2.0 moles of hydrogen per mole of ethylene in the gas phase. Any gas inert to the catalyst and reactants can also be present in the gas stream.

10 In one embodiment, the catalyst of the invention exhibits high activity for polymerization of ethylene and higher  $\alpha$ -olefins and allows the synthesis of ethylene polymers and copolymers with a relatively narrow molecular weight distribution and homogeneous branching distribution. The

15 molecular weight distribution is determined as MFR which ranges from 15 to 25, in polymerizations of the invention. Branching distribution in ethylene copolymers is evaluated on the basis of the resin's melting point. Relatively homogeneous branching distribution is one which the melting point ranges from 100°C to 120°C, depending on comonomer composition. In this embodiment, the catalyst of the invention contains only one source of transition metal, the metallocene.

Particularly, the copolymer products contain 0.1 to 2 ppm of Zr. The product has an average particle size of 0.015-0.035 inches (0.38 to 0.89 mm), settled bulk density from 25 to 36 lb/ft<sup>3</sup> (400 to 577 kg/m<sup>3</sup>). The particles of product are spherical. The narrow molecular weight distribution low density copolymers have been produced with MI of between 1 and 0.01. The low density products of the invention exhibit a MI which can 30 range from 0.01 to 5, preferably from 0.5 to 4, and most preferably 0.8 to 2.0. The low density products of the invention exhibit a melt flow ratio (MFR) of 14 to 25 preferably from 14 to 20; products with MFR ranging from 16 to 18 have been made; MFR is the ratio I21/I2 [wherein I21 is measured at 190°C] 35 in accordance with ASTM D-1238, Condition F, and I2 is measured in accordance with ASTM D-1238, Condition E]. When fabricated into films, the films of the copolymers exhibit balanced tear

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strength, as measured by ASTM D-1922. Furthermore the LLDPE of the invention exhibits Dart Drop Impact values as measured by ASTM D-1709 of greater than 800. The products of the catalysis with the catalyst of the invention can be used as films which are substantially free of gels. The films exhibit very low haze values as measured by ASTM D-1003, preferably in the range of 3 to 10, more preferably from 5 to 7.

#### EXAMPLES

10 MAO (methaluminoxane) is commercially available from Ethyl Chemical and WITCO (previously Schering Berlin) as 10 weight percent and 30 weight percent solutions, which were the sources of MAO used in the Examples.

15 Catalyst Preparation:

(A) 493g of silica (Davison 955), dehydrated at 250°C, was reacted with a solution of 6.986 g of  $(n\text{-butylCp})_2\text{ZrCl}_2$  dissolved in 670 grams of MAO in toluene. Gas evolution was observed. The MAO solution contained 13.7 wt% Al. The Al/Zr

20 ratio was 200:1. The catalyst was dried under flowing  $\text{N}_2$  at 45°C for 5 hours, and was sieved to remove any particles larger than 150 microns. The catalyst contained 9.2 wt% Al and 0.17 wt% Zr.

(B) 514g of silica (Davison 955), dehydrated at 600°C, was reacted with a solution of 7.272 g of  $(n\text{-butylCp})_2\text{ZrCl}_2$  dissolved in 685 g of MAO in toluene. Gas evolution was observed. The MAO solution contained 14.1 wt% Al. The Al/Zr ratio was 200:1. The catalyst was dried under flowing  $\text{N}_2$  at 45°C for 5 hours, and was then sieved to remove any particles

30 larger than 150 microns. The catalyst contained 11.0 wt% Al and 0.19 wt% Zr.

(C) 475g of silica (Davison 955), dehydrated at 600°C, was slurried in isopentane and was then treated with 510  $\text{cm}^3$  of a TMA solution (1.4M). After all the TMA solution was added, the

35 slurry was dried to a fine free-flowing white powder. To this white powder, a solution of 6.727 grams of  $(n\text{-butylCp})_2\text{ZrCl}_2$  and 627 grams of MAO in toluene was added slowly to the slurry. The

(D) 486g of silica (PQ 988), dehydrated at 600°C, was slurried in isopentane and was then treated with 517 cm<sup>3</sup> of a TMA solution (1.4M). After all the TMA solution was added, the slurry was dried to a fine free-flowing white powder. To this white powder, a solution of 6.90 grams of (n-butylCp)<sub>2</sub>ZrCl<sub>2</sub> and 650 grams of MAO in toluene was added. The MAO solution contained 14.1 wt% Al. The Al(in MAO)/Zr ratio was 200:1. The catalyst was dried under flowing N<sub>2</sub> at 45°C for 5 hours, and was then sieved to remove any particles larger than 150 microns. The catalyst contained 14.15 wt% Al and 0.22 wt% Zr. (1)

MAO in toluene was added slowly to the slurry. The MAO solution was 13.2 wt% Al. The Al(in MAO)/Zr ratio was 200:1. The catalyst was dried under flowing N<sub>2</sub> at 60°C for 24 hours, and was then sieved to remove any particles larger than 150 microns. The catalyst contained 13.10 wt% Al and 0.20 wt% Zr.

35 (G) - 497g of silica (Davison 955), dehydrated at 600°C, was reacted with a solution of 3.540 g of (n-butylCp)<sub>2</sub>ZrCl<sub>2</sub> dissolved in 650 g of MAO in toluene. Gas evolution was

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observed. The MAO solution contained 14.1 wt% Al. The Al/Zr ratio was 400:1. The catalyst was dried under flowing N<sub>2</sub> at 45°C for 5 hours, and was then sieved to remove any particles larger than 150 microns. The catalyst contained 9.85 wt% Al and 5 0.09 wt% Zr.

(H) 499g of silica (Davison 955), dehydrated at 600°C, was reacted with a solution of 3.533 g of (n-butylCp)<sub>2</sub>ZrCl<sub>2</sub> dissolved in 335 g of MAO in toluene. Gas evolution was observed. The MAO solution contained 14.1 wt% Al. The Al/Zr ratio was 200:1. The catalyst was dried under flowing N<sub>2</sub> at 45°C for 5 hours, and was then sieved to remove any particles larger than 150 microns. The catalyst contained 5.96 wt% Al and 0.10 wt% Zr.

(I) 493g of silica (Davison 955), dehydrated at 600°C, was reacted with a solution of 13.972 g of (n-butylCp)<sub>2</sub>ZrCl<sub>2</sub> dissolved in 674 g of MAO in toluene. Gas evolution was observed. The MAO solution contained 13.7 wt% Al. The Al/Zr ratio was 200:1. The catalyst was dried under flowing N<sub>2</sub> at 45°C for 5 hours, and was then sieved to remove any particles larger than 150 microns. The catalyst contained 9.46 wt% Al and 0.32 wt% Zr.

(J) 503g of silica (Davison 955), dehydrated at 600°C, was reacted with a solution of 7.112 g of (n-butylCp)<sub>2</sub>ZrCl<sub>2</sub> dissolved in 667 g of MAO in toluene. Gas evolution was observed. The MAO solution contained 13.7 wt% Al. The Al/Zr ratio was 200:1. The catalyst was dried under flowing N<sub>2</sub> at 45°C for 5 hours, and was then sieved to remove any particles larger than 150 microns. The catalyst was further reacted with a solution of 4.079 g of (n-butylCp)<sub>2</sub>ZrCl<sub>2</sub> dissolved in 407 g of MAO in toluene. The catalyst was again dried under N<sub>2</sub> at 45°C for 5 hours. The catalyst contained 12.85 wt% Al and 0.25 wt% Zr.

(K) 505g of silica (Davison 955), dehydrated at 250°C, was reacted with a solution of 7.148 g of (n-butylCp)<sub>2</sub>ZrCl<sub>2</sub> dissolved in 698 g of MAO in toluene. Gas evolution was observed. The MAO solution contained 13.7 wt% Al. The Al/Zr ratio was 200:1. The catalyst was dried under flowing N<sub>2</sub> at

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45°C for 5 hours, and was then sieved to remove any particles larger than 150 microns.

(L) 483g of silica (Davison 952-1836), dehydrated at 250°C, was reacted with a solution of 6.710 g of bis(tetrahydroindenyl) zirconium dichloride dissolved in 655 g of MAO in toluene. Gas evolution was observed. The MAO solution contained 13.7 wt% Al. The Al/Zr ratio was 200:1. The catalyst was dried under flowing N<sub>2</sub> at 45°C for 5 hours, and was then sieved to remove any particles larger than 150 microns.

10

### Slurry Polymerization

Polymerization was conducted in a 2 liter slurry reactor. One liter polymerization grade heptane, 100 cm<sup>3</sup> 1-hexene, and 2 cm<sup>3</sup> tri-isobutyl aluminum (TIBA, 25 wt% in heptane) were added to the reactor at room temperature. The reactor contents were then agitated at 900 rpm and heated up to 70°C. Ethylene was then added to maintain a constant pressure of 125 psig (0.86 MPa) in the reactor. About 80 to 120 mg of a catalyst from the examples was injected into the reactor. Results are shown in Table 1, 2 and 3 (located at the end of the description).

Table 1 shows that catalyst (A) is the most active catalyst. Catalyst (A) uses a Davison 955 silica dehydrated at 250°C and therefore has the most reactive surface with 1.8 mmole hydroxyl group per gram of silica. Catalyst (B) is the second most active using Davison 955 silica dehydrated at 600°C with 0.72 mmole of hydroxyl group per gram of silica. Thus, the reaction between the metallocene/methylaluminoxane solution with hydroxyl groups on the silica surface is a very important step in producing a highly active catalyst.

Catalyst (C), (D), and (E) are examples that use either Davison 955 (for catalyst (C)) or PQ 988 silica (for catalyst (D) and (E)). The silicas were dehydrated at 600°C and then treated with trimethylaluminum to remove all the hydroxyl group on the silica surface. Without the reactive hydroxyl groups on the surface, all three of these catalysts showed poorer activity.

Furthermore, catalyst (E) was prepared using additional

toluene (2500 cm<sup>3</sup>) to slurry the silica before drying at 60°C for 24 hours. This example illustrates that excess solvent during the preparation step and long drying time at higher temperature (60°C rather than 45°C) produce a very poor catalyst.

Table 2 shows that wide ranges of loadings of methylaluminoxane and metallocene can be used to react with Davison 955 silica dehydrated at 600°C. The loadings are summarized below:

	Per gram silica		Al/Zr
	mmole Al	mmole Zr	
(F)	3.5	0.035	200
(G)	7.0	0.018	400
15 (H)	3.5	0.018	200
(I)	7.0	0.070	100
(J)	11.0	0.055	200

Furthermore, Catalyst (J) shows that multiple-step dry-impregnation (incipient wetness method) of the catalyst also produces a high activity catalyst.

Table 3 shows an example where bis(tetrahydroindenyl) zirconium dichloride can be used instead of bis(n-butylcyclopentadienyl) zirconium dichloride. Other metallocene compounds can also be used.

#### Semi-Batch Gas Phase Polymerization

A two-liter stainless steel autoclave was fitted with an anchor-type agitator. It was cleaned and purged with nitrogen at 100°C to remove air and moisture. 20 gram of 955-600 silica, treated with 2 cm<sup>3</sup> of trimethylaluminum (TMA, 15 wt% in heptane) were blended with 40 to 150 mg of a catalyst under nitrogen. The entire content was charged into the autoclave under nitrogen. 10 cm<sup>3</sup> of heptane and 5 cm<sup>3</sup> of hexene were injected into the reactor. The reactor temperature was set at 80°C and the reactor pressure was maintained at 175 psig (1.20 MPa) by a continuous supply of ethylene. Small portions of hexene were



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injected into the reactor at regular intervals to replenish the amount consumed. Polymerization was stopped by injection of methanol when sufficient quantity of the polymer was made. Results are shown in Table 4.

5 Table 4 shows that these catalysts can polymerize alpha-olefins in a stirred-bed gas-phase reactor. Catalyst (E) is much less active than catalyst (B).

#### Fluid Bed Gas Phase Reactor

10 These catalysts were also tested in a pilot plant fluid-bed reactor (13 inch (0.33m) ID and bed volume of 4.0 ft<sup>3</sup> (0.11 m<sup>3</sup>)). Polymerizations were carried out typically at 77.5°C, with 180-255 psi (1.24 to 1.76 MPa) of ethylene, and 0.016 to 0.021 hexene to ethylene mole ratio. The fluidized gas velocity  
 15 was 1 to 2 ft/s (0.3 to 0.61 m/s). The results are summarized in Tables 5 and 6.

20 All of these catalysts ran well in the fluid bed reactor. Although the catalyst ash varied among these formulations, good fluid bed operation was observed in all cases. Fractional melt index material can be made by adding oxygen to the reactor in trace levels or by changing the catalyst formulation. Similarly, addition of isopentane was determined to decrease the melt index in this technology. The effects of isopentane, oxygen and other impurities such as carbon dioxide, carbon  
 25 monoxide, etc. are unique in this technology. We use these impurities for making desired Melt index products.

The resin settled bulk density in all cases is between 28 to 34 lb/ft<sup>3</sup> (450 to 546 kg/m<sup>3</sup>) and the fines (defined as particle smaller than 120 Mesh) level is below 5%.

30 Table 5 shows that catalyst (A) and (B) using silica with reactive surface have much higher activity than catalyst (C), (D), and (E) which do not use silica with a reactive surface.

Table 6, similar to Table 3, show the ranges of methyaluminoxane and metallocene loadings that can be used.

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# **PRODUCT PROPERTIES**

## **1. Resin Characteristics.**

When compared to the standard ethylene-hexene copolymer prepared with the commercial Ziegler catalysts, the resins produced herein via the gas phase process exhibited the following characteristics: (1) narrower molecular weight distribution, (2) more uniform short chain branching distribution, (3) lower melting point (4) lower extractables, and (5) lower haze.

10 An example of the key resin characteristics of a 1.0 I2, 0.918 density resin is shown below:

## **LLDPE resin Characteristics**

1.0 I2, 0.918 density

15	Commercial	Mobil's
Property	Ziegler	Metallocene

Mw/Mn 4.5 2.6

MFR 28 18

20 Melting point/°C 125 115

## **2. End-use property**

The LLDPE resins can be processed readily on commercial equipment without modification. They also offer superior properties compared to those resins produced using a commercial Ziegler/Natta catalyst. An example is given below:

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LLDPE Film Property Comparison

1.0 I21, 0.918 density

2:1 BUR, 250 lb/hr

5	Commercial	Mobil's
Property	Ziegler	Metallocene
Melt Pressure/psi(MPa)	5000 (34)	5500 (38)
Bubble Stability	Very Good	Very Good
10 MD Modulus/10 <sup>4</sup> psi(MPa)	2.8 (193)	2.5 (172)
Dart Drop/g	180-450	>800
MD Tear/g/mil(g/μ)	350-450 (13.8 to 17.7)	370 (14.6)
Extractables, %	2.5	0.6
Haze, %	18	5-7

15

PRODUCT SCOPING

Using catalyst formulations similar to catalyst A, we have done preliminary product scoping in the fluid-bed reactor. Products at densities ranging from 0.915 to 0.962 g/cm<sup>3</sup> by varying comonomer level (hexene or butene) and melt index ranging from 0.5 to 250. The product can be made at significantly higher or lower melt index (greater than 500 or less than 0.01) if necessary; this is achieved by varying the reactor temperature, ethylene partial pressure, isopentane, oxygen (or carbon dioxide, carbon monoxide) and hydrogen. Similarly, it is possible to achieve lower density than 0.915 g/cm<sup>3</sup> (0.905 g/cm<sup>3</sup> or lower) and higher densities than 0.962 if necessary.

The following Examples 1A-3A are from US patent application serial no 08/036,796, filed March 25, 1993.

The properties of the polymers produced in the Examples were determined by the following test methods:

Density ASTM D-1505 - a plaque is made and conditioned for one hour at 100°C to approach equilibrium crystallinity. Measurement for density is then made in a density gradient

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column; reported as g/cm<sup>3</sup>.

Melt Index  
5 (MI), I2

ASTM D-1238 - Condition E

Measured at 190°C - reported as grams per 10 minutes.

High Load  
10 Melt Index

ASTM D-1238 - Condition F

Measured at 10.5 times the weight used in (HLMI), I21 the melt index test above.

Melt Flow  
Ratio (MFR)

I21/I2

15

EXAMPLE 1A

Example 1A

Raw materials used in catalyst preparation included 505 g of Davison 952-1836 silica, 698 g of methylaluminoxane in 20 toluene solution (30 wt% MAO), 7.148 g of bis(n-butylcyclopentadienyl) zirconium dichloride.

The steps of the catalyst preparation are set forth below:

1. Dehydrate the 955 silica at 250°C for 4 hours using air to purge. Then purge with nitrogen on cooling.
2. Transfer the silica to a mix-vessel.
3. Add 7.148 g of bis(n-butylcyclopentadienyl) zirconium dichloride and 698 g of methylaluminoxane to a bottle.
4. Agitate the catalyst solution in the bottle until the metallocene dissolves in the MAO solution.
5. Transfer the MAO and metallocene solution into the mix-vessel containing the dehydrated 955 silica slowly while agitating the silica bed vigorously to make sure that the catalyst solution is well dispersed into the silica bed.
6. After the addition, continue to agitate the catalyst for 0.5 hours.

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7. Start drying the catalyst by purging with nitrogen for 5 hours at 45°C.

8. Sieve the catalyst to remove particles larger than 150 micron.

5 9. The catalyst has the following analysis:

Yield = 914 g catalyst (from 500 g of silica)

Al = 10 wt%

Zr = 0.2 wt%

Example 2A

10 To produce a polymer for low density film, 0.918 g/cm<sup>3</sup>, 1 MI, 17 MFR, in a fluid bed gas phase reactor the following process conditions were employed.

Process Conditions:

15	Fluidization velocity	1.7 ft/s (0.52 m/s)
	Residence time	2.5 hours
	Temperature	77.5 °C
	Ethylene	180 psi (1.24 MPa)
	Hexene	3.6 psi (24.8 KPa)
20	Isopentane	50 psi (345 KPa)
	Carbon dioxide	1.1 ppm
	Ash	200 to 250 ppm

The catalyst was that of Example 1A.

Example 3A

25 To produce a polymer for cast film of 0.918 g/cm<sup>3</sup> density, 2.5 MI, 16 MFR, the following process conditions were employed:

	Fluidization velocity	1.7 ft/sec (0.52 m/s)
	Residence time	2.5 hours
	Temperature	77.5 °C
30	Ethylene	180 psi (1.24 MPa)
	Hexene	3.6 psi (24.8 KPa)
	Isopentane	38 psi (262 KPa)
	Ash	100 ppm

The catalyst was that of Example 1A.

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Reacting the catalyst by pumping with nitrogen

Table 1

Cat	Reaction	Catalyst	Zr					
Cat wt	Time	Yield	Activity	Activity	Density	MI	MFR	
(g)	(min)	(g)	(g/g-cat/h)	(Kg/g-Zr/hr)				
5 (A)	0.067	52	174	2500	1470	0.914	1.17	18.3
(B)	0.116	65	163	1100	580	0.914	1.09	18.1
(C)	0.080	60	65	810	450	0.914	0.75	19.2
(D)	0.111	54	44	360	160	0.915	0.62	19.6
(E)	0.114	58	11	80	40			

10

Table 2

Cat	Reaction	Catalyst	Zr					
Cat wt	Time	Yield	Activity	Activity	Density	MI	MFR	
(g)	(min)	(g)	(g/g-cat/h)	(Kg/g-Zr/hr)				
15 (F)	0.079	60	127	1610	770	0.913	1.01	18.2
(G)	0.113	60	69	610	680	0.915	1.00	19.1
(H)	0.078	60	76	980	980	0.912	0.61	18.4
(I)	0.073	60	131	1800	670	0.916	1.48	18.0
(J)	0.085	56	207	2600	1040	0.916	1.56	18.6

20

Table 3

Cat	Reaction	Catalyst	Zr					
Cat wt	Time	Yield	Activity	Activity	Density	MI	MFR	
(g)	(min)	(g)	(g/g-cat/h)	(Kg/g-Zr/hr)				
25 (L)	0.084	60	62	750		0.910		

Table 4

Cat	Reaction							
Cat wt	Time	Yield	Activity	Density	MI	MFR		
(g)	(min)	(g)	(g/g/h)	(g/cm <sup>3</sup> )				
(B)	0.098	34	132	1340				
(E)	0.107	57	37	580				

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Table 5

Cat	Oxygen (ppm)	Isopentane (psi [KPa])	Cat ash (ppm)	Al (ppm)	Zr (ppm)	Density (g/cm <sup>3</sup> )	MI
(A)	0.2	52 [359]	344	40	0.8	0.917	0.6
5 (A)	0.0	51 [352]	206	27	0.5	0.917	1.1
(B)	0.0	43 [296]	331	44	0.5	0.917	1.1
(C)	0.0	53 [365]	596	73	1.3	0.917	1.5
(D)	0.0	0.0 [0.0]	750	105	1.8	0.930*	2.3
(E)	Activity too low (see Table 1)						

10

\*Hexene to ethylene gas ratio of 0.009.

Reactor temperature 85°C.

Table 6

15 Cat	Oxygen (ppm)	Isopentane (psi [KPa])	Cat ash (ppm)	Al (ppm)	Zr (ppm)	Density (g/cm <sup>3</sup> )	MI
(F)	0.0	43 [296]	806	50	2.0	0.917	0.6
(G)	0.0	43 [296]	782	92	1.0	0.918	0.8
(H)	0.0	38 [262]	878	36	1.2	0.919	0.6
20 (I)	0.0	53 [365]	287	15	0.7	0.917	0.8
(J)	0.0	50 [345]	295	41	0.9	0.917	1.0
(K)	0.0	48 [331]	103	18	0.4	0.918	1.9

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# Claims

1. An olefin polymerization or copolymerization catalyst comprising particles, said particles comprising silica, a transition metal and aluminum, wherein:

(a) wherein said silica is amorphous, porous, has a pore volume of 0.1 to 5 cm<sup>3</sup>/g and has a concentration of silanol groups wherein the concentration of silanol groups is at least 0.7 mmole per gram of silica;

(b) said transition metal and said aluminum being provided by a mixture of a metallocene and an alumoxane; and

(c) the total volume of said metallocene and said alumoxane is less than or equal to the total pore volume of the silica.

2. A catalyst according to claim 1, wherein the metallocene has the formula, Cp<sub>m</sub>MA<sub>n</sub>B<sub>p</sub>, wherein Cp is a cyclopentadienyl or a substituted cyclopentadienyl group, m is 1 or 2, M is zirconium or hafnium and each of A and B is selected from the group consisting of a halogen atom, a hydrogen atom and an alkyl group, providing that m+n+p is equal to the valence of the metal M.

3. A catalyst according to claim 1, wherein the metallocene is bis (n-butylcyclopentadienyl) zirconium dichloride

4. A catalyst according to claim 1, wherein the metallocene is (tetrahydroindenyl) zirconium dichloride

5. A catalyst according to Claim 1, wherein the metallocene is selected from the group consisting of bis(cyclopentadienyl)metal dihalides, bis(cyclopentadienyl)metal hydridohalides, bis(cyclopentadienyl)metal monoalkyl monohalides,



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bis(cyclopentadienyl)metal dialkyls and bis(indenyl)metal dihalides.

6. A catalyst according to Claim 1, wherein the metallocene is selected from the group consisting of bis(cyclopentadienyl)zirconium dichloride, bis(cyclopentadienyl)hafnium dichloride, bis(cyclopentadienyl)zirconium dimethyl, bis(cyclopentadienyl)hafnium dimethyl, bis(cyclopentadienyl)zirconium hydrido-chloride, bis(cyclopentadienyl)hafnium hydrido-chloride, bis(n-butylcyclopentadienyl)zirconium dichloride, bis(n-butylcyclopentadienyl)hafnium dichloride, bis(n-butylcyclopentadienyl)zirconium dimethyl, bis(n-butylcyclopentadienyl)hafnium dimethyl, bis(n-butylcyclopentadienyl)zirconium hydrido-chloride, bis(n-butylcyclopentadienyl)hafnium hydrido-chloride, bis(pentamethylcyclopentadienyl)zirconium dichloride, bis(pentamethylcyclopentadienyl)hafnium dichloride, bis(n-butylcyclopentadienyl)zirconium dichloride, cyclopentadienyl-zirconium trichloride, bis(indenyl)zirconium dichloride, bis(4,5,6,7-tetrahydro-1-indenyl)zirconium dichloride, and ethylene-[bis(4,5,6,7-tetrahydro-1-indenyl)] zirconium dichloride.

7. A catalyst according to claim 1, wherein the alumoxane has the formula:

- (a)  $R-(Al(R)-O)_n-AlR_2$  for oligomeric, linear alumoxanes; or  
(b)  $(-Al(R)-O-)_m$  for oligomeric cyclic alumoxane

8. A catalyst according to Claim 1, wherein the aluminoxane is methylalumoxane (MAO).

9. A catalyst according to claim 1, wherein the ratio of aluminum to transition metal ranges from 70 to 350.

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10. A catalyst according to Claim 1, wherein ratio of aluminum to transition metal is 100 to 200.

11. A catalyst according to claim 1, wherein said particles have a particle size in the range of 1 to 500 microns.

12. A catalyst according to Claim 1, wherein the particles have a particle size in the range of 1 to 250 microns.

13. A catalyst according to Claim 1, wherein the concentration of silanol groups is greater than 0.7 and up to 2.5 mmole per gram of silica.

14. A catalyst according to Claim 1, wherein the concentration of silanol groups is between 1.7 and 1.9 mmole per gram of silica.

15. A process for preparing a catalyst according to claim 1, said process comprising:

(a) providing an amorphous porous hydrated silica and dehydrating said silica at a dehydration temperature of less than 300°C to provide a dehydrated silica having a silanol concentration of at least 0.7 mmoles per gram silica,

(b) providing a volume of a mixture of said metallocene and said aluminoxane, and contacting said silica with said volume of said mixture, to allow impregnation of the pores of said silica with said mixture; and

(c) recovering an activated catalyst.

16. A process according to Claim 15, wherein said mixture is a solution which has a volume equal to or less than the total pore volume of said silica and wherein said solution is employed to impregnate said silica and wherein said solution further comprises a single solvent which is a solvent for said aluminoxane.

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17. A process according to Claim 15, wherein, after said contacting, solvent is removed from pores of said silica at a temperature which does not exceed 100°C.

18. A process according to Claim 17, wherein said temperature at which the solvent is removed does not exceed 80°C.

19. A process according to Claim 17, wherein said temperature at which the solvent is removed is in the range of 40 to 50°C.

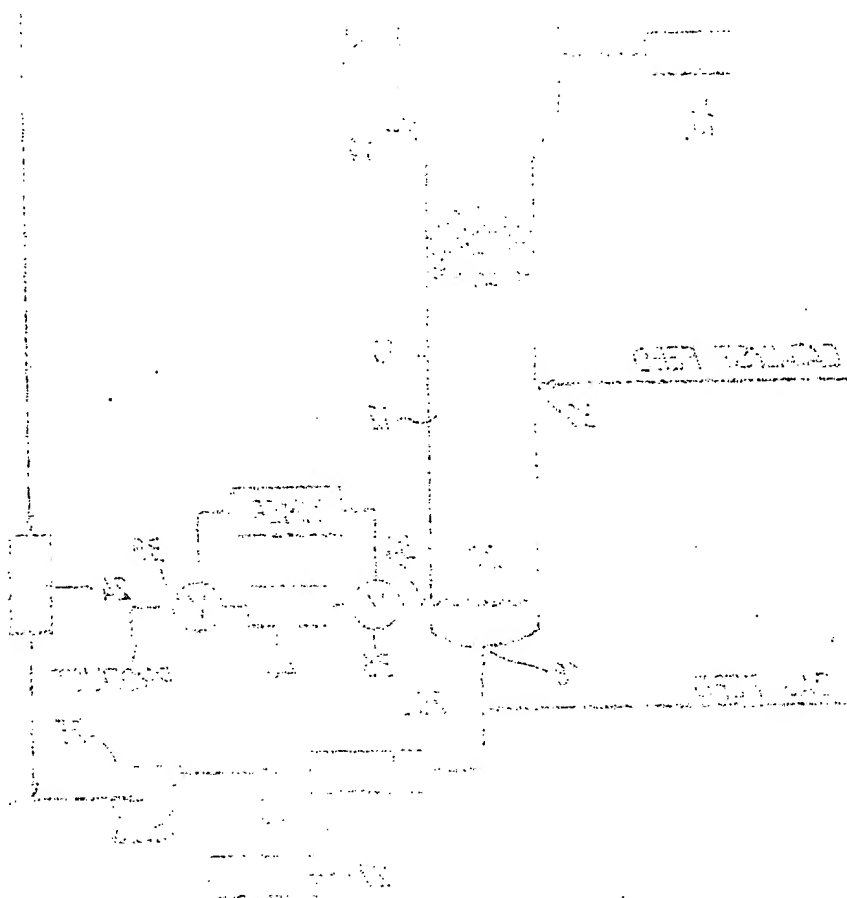


FIG. 1

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GAS RECYCLE

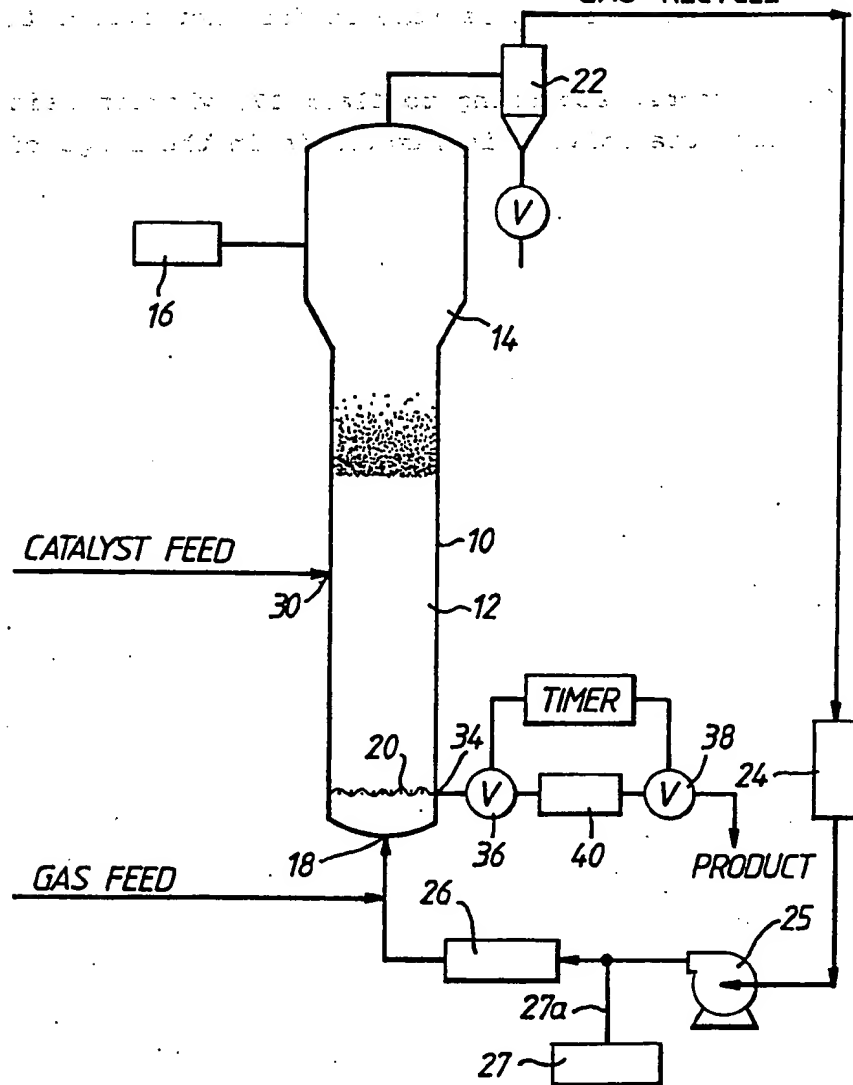


Fig.1

## INTERNATIONAL SEARCH REPORT

International application No.  
PCT/US94/07232**A. CLASSIFICATION OF SUBJECT MATTER**

IPC(5) :C08F 4/646

US CL :502/104, 107, 113, 115, 117, 120; 526/114, 116, 120

According to International Patent Classification (IPC) or to both national classification and IPC

**B. FIELDS SEARCHED**

Minimum documentation searched (classification system followed by classification symbols)

U.S. : 502/104, 107, 113, 115, 117, 120; 526/114, 116, 120

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

APS:

SEARCH ITEMS: SILICA, SILANOL, METALLOCENE?, ALUMINOXANE OR ALUMOXANE, OR METHYLALUMINOXANE, 502/CLAS, SILICA SUPPORT.

**C. DOCUMENTS CONSIDERED TO BE RELEVANT**

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US, A, 4,914,253 (CHANG) 03 APRIL 1990, ALL PAGES	1-12, 15-19
X	US, A, 5,001,205 (HOEL) 19 MARCH 1991, ALL PAGES	1-12,15-19
X	US, A, 5,026,797 (TAKAHASHI) 25 JUNE 1991 ALL PAGES	1-12,15-19
T	US, A, 5,332,706 (NOWLIN ET AL.) 26 JULY 1994, ALL PAGES	1-19
X	EP, A, 515,132 (UEDA ET AL.) 25 NOVEMBER 1992, ALL PAGES	1-19



Further documents are listed in the continuation of Box C.



See patent family annex.

\*A\*

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document referring to an oral disclosure, use, exhibition or other means

\*P\*

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\*T\*

later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

\*X\*

document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

\*Y\*

document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art

\*Δ\*

document member of the same patent family

Date of the actual completion of the international search

25 AUGUST 1994

Date of mailing of the international search report

SEP 08 1994

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